TECHNICAL MEMORANDUM

HERBICIDE MONITORING PROGRAM FOR
N-METHYLFORMAMIDE AND FLURIDONE (SONAR(R))

by

RICHARD J. PFEUFFER

November 1990

Water Quality Division
Department of Research and Evaluation
South Florida Water Management District
West Palm Beach, Florida

ABSTRACT

Photolysis is one of the major degradation pathways of the aquatic herbicide fluridone. One of the photodegradation products, N-methylformamide (NMF), was monitored in a field application in Lake Kissimmee to determine if this toxic compound would be produced during a lake application of the commercial formulations of fluridone. None of the water samples collected up to 49 days after application had any detectable quantities of NMF at a minimum detection limit of 5 ppb. NMF does not appear to be a concern when fluridone is utilized in a lake application according to labeled rates. The levels of fluridone detected in the water samples reflect what would be expected for this compound. The field half-life of seven days was analogous to that reported in a similar monitoring program on Lake Okeechobee.

ACKNOWLEDGEMENTS

EXECUTIVE SUMMARY

Fluridone (1-methyl-3-phenyl-5-[3-(trifluoromethyl)phenyl]-4(1H)-pyridinone), the active ingredient of Sonar[R], is one of the herbicides used by the South Florida Water Management District (SFWMD) for the control of exotic nuisance aquatic plants. During FY87/88, the SFWMD utilized 1,734 gallons of Sonar[R] AS (aqueous suspension) and 5,867 pounds of Sonar[R] SRP (slow release pellet) in an attempt to control hydrilla (Hydrilla verticillata) in Lake Okeechobee, Lake Kissimmee, Lake Hatchineha, and East Lake Tohopekaliga.

One concern about aquatic herbicides is the potential environmental impact caused by their utilization. The impact can come from the effects caused by either the active ingredient or any degradation product(s). Fluridone has been monitored by the SFWMD in a field application on Lake Okeechobee with no apparent impacts from the active ingredient, as dissipation and degradation proceeded as anticipated. However, one of the potential degradation products of fluridone, N-methylformamide (NMF), is exceedingly toxic to humans. The potential exists that if any NMF is generated after an application of fluridone, it could enter the human body through consumption of drinking water and/or skin contact through recreational uses. To ascertain the risk of NMF exposure, this study sought to measure NMF levels in lake water following an application of the commercial formulations of fluridone.

Twenty-five 25-acre (10.1 hectare) treatment plots were selected by the SFWMD's Operations and Maintenance Department in Lake Kissimmee for the control of hydrilla. Treatment plots in the northern part of Lake Kissimmee were used as the study area. The 19 treatment plots in the southern part of the lake were sprayed the week before. Fluridone was aerially applied on June 15, 1988 at three of

the northern sites with the Sonar$^{(R)}$ AS (aqueous suspension) formulation at 2.5 quarts per acre (2.8 kg of active ingredient per hectare). The fourth site received the Sonar$^{(R)}$ SRP (slow release pellet) formulation on June 20, at 40 pounds per acre (2.2 kg of active ingredient per hectare). Surface water and sediment samples were taken the day before spraying, immediately after spraying, 1-1/2 hours after spraying, the following day, and approximately once per week for six weeks. The last sediment samples were taken approximately 16 weeks after spraying. Fluridone was analyzed in both water and sediment samples. NMF was analyzed in the water samples up to 49 and 44 days after treatment at the aqueous suspension and pellet formulation sites, respectively.

Although photolysis is one of the major degradation pathways for fluridone and NMF is one of the photodegradation products, NMF was not found in the water in field applications of fluridone. NMF does not appear to be a concern when fluridone is utilized in a lake application according to labeled rates.

The levels of fluridone detected in the water samples reflect what would be expected for this compound. The field half life of seven days was comparable to that reported in a similar monitoring program on Lake Okeechobee and reported in the literature.

Detectable concentrations of fluridone were found in the sediment before spraying began at the study site. Suspected sources could be previous applications of fluridone in Lake Kissimmee.

CONTENTS

INTRODUCTION

Fluridone(1-methyl-3-phenyl-5-[3-(trifluoromethyl)phenyl]-4(1H)-pyridinone), the active ingredient of Sonar[R], is one of the herbicides used by the South Florida Water Management District (SFWMD) for the control of exotic nuisance aquatic plants. During FY87/88, the SFWMD utilized 1,734 gallons of Sonar[R] AS (aqueous suspension) and 5,867 pounds of Sonar[R] SRP (slow release pellet) in an attempt to control hydrilla (Hydrilla verticillata) in Lake Okeechobee, Lake Kissimmee, Lake Hatchineha, and East Lake Tohopekaliga (Gordon Baker, pers. comm.). The aqueous suspension is formulated at four pounds active ingredient per gallon and the slow release clay pellet at two pounds active ingredient per 40-pound container.

One concern about aquatic herbicides is the potential environmental impact caused by their utilization. The impact can come from the effects caused by either the active ingredient or any degradation product(s). Fluridone has been monitored by the SFWMD in a field application on Lake Okeechobee with no apparent impacts from the active ingredient, as dissipation and degradation proceeded as anticipated (Pfeuffer, 1988). However, one of the potential degradation products of fluridone, N-methylformamide (NMF), is exceedingly toxic to humans (Barlow and Sullivan, 1982; Kennedy, 1986).

Saunders and Mosier (1983) identified NMF as a persistent photodegradation product in a laboratory study. The generation of NMF "increased steadily" throughout their photolysis experiment in both distilled and lake water and "showed no significant degradation." Some research suggests NMF's toxicity may operate on a nonthreshold mechanism where there is no safe level of exposure, i.e., any exposure, no matter how small, offers some probability of adverse effects. Barlow and Sullivan

(1982) concluded that NMF did not show a "no-effect level" (the dosage or exposure level at which no toxicologically significant adverse effect(s) can be detected) after a review of the literature concerning reproductive effects. However, Kennedy (1986) reported a "no-effect level" of 10 mg/Kg for NMF in rabbits for fetotoxicity (a compound-induced toxic effect on the fetus during the latter phase of pregnancy) and teratogenicity (production of irreversible birth defects or anatomical or functional disorders as a result of an effect on the developing embryo or fetus by a compound which can cross the placenta). Although the exact level of toxicity is unclear, NMF is a toxic compound to humans. Information on the toxicity of NMF to fish, birds, or invertebrates has not been reported. The potential exists that if any NMF is generated during an application of fluridone, it could enter the human body through consumption of drinking water and/or through skin contact during recreational uses. To ascertain the risk of NMF exposure, this study sought to measure NMF levels in lake water following an application of the commercial formulations of fluridone.

MATERIALS AND METHODS

Twenty-five 25 acre (10.1 hectare) treatment plots in Lake Kissimmee were selected by the SFWMD's Operations and Maintenance Department for the control of hydrilla. Two treatment plots in the northern part of Lake Kissimmee were sampled for this study (Figure 1). This area was chosen as it is believed to be isolated from the influences of water movement compared to the other hydrilla infested treatment areas. The 19 treatment areas in the southern part of the lake were sprayed the week before.

Fluridone was aerially applied on June 15, 1988 at three of the northern sites with the Sonar(R) AS (aqueous suspension) formulation at 2.5 quarts per acre (2.8 kg of active ingredient per hectare). The fourth site received the Sonar(R) SRP (slow release pellet) formulation on June 20, at 40 pounds per acre (2.2 kg of active ingredient per hectare). The water depth at the time of application was approximately seven feet (2.1 meters). Three sites within each formulation's treatment area were marked with floating markers and sampled at the frequencies shown in Tables 1 and 2. The control site was located approximately one mile from the treatment areas, outside the normal range of dispersal (West, et al., 1983; Pfeuffer, 1988). Both water column and sediment samples were collected in glass containers provided by the contract laboratory (PBS&J Environmental Laboratories, Orlando, Florida) that were specifically prepared for herbicide residue sampling. The water column samples were surface grab samples. The top 2.5 inch (6.35 centimeters) layer of sediment was obtained using a three-inch (7.62 centimeter) diameter corer. Duplicate samples were obtained within the application area as well as the control site for quality assurance. All samples were stored on ice or refrigerated until analyzed. Fluridone was analyzed in both the water and sediment samples. NMF
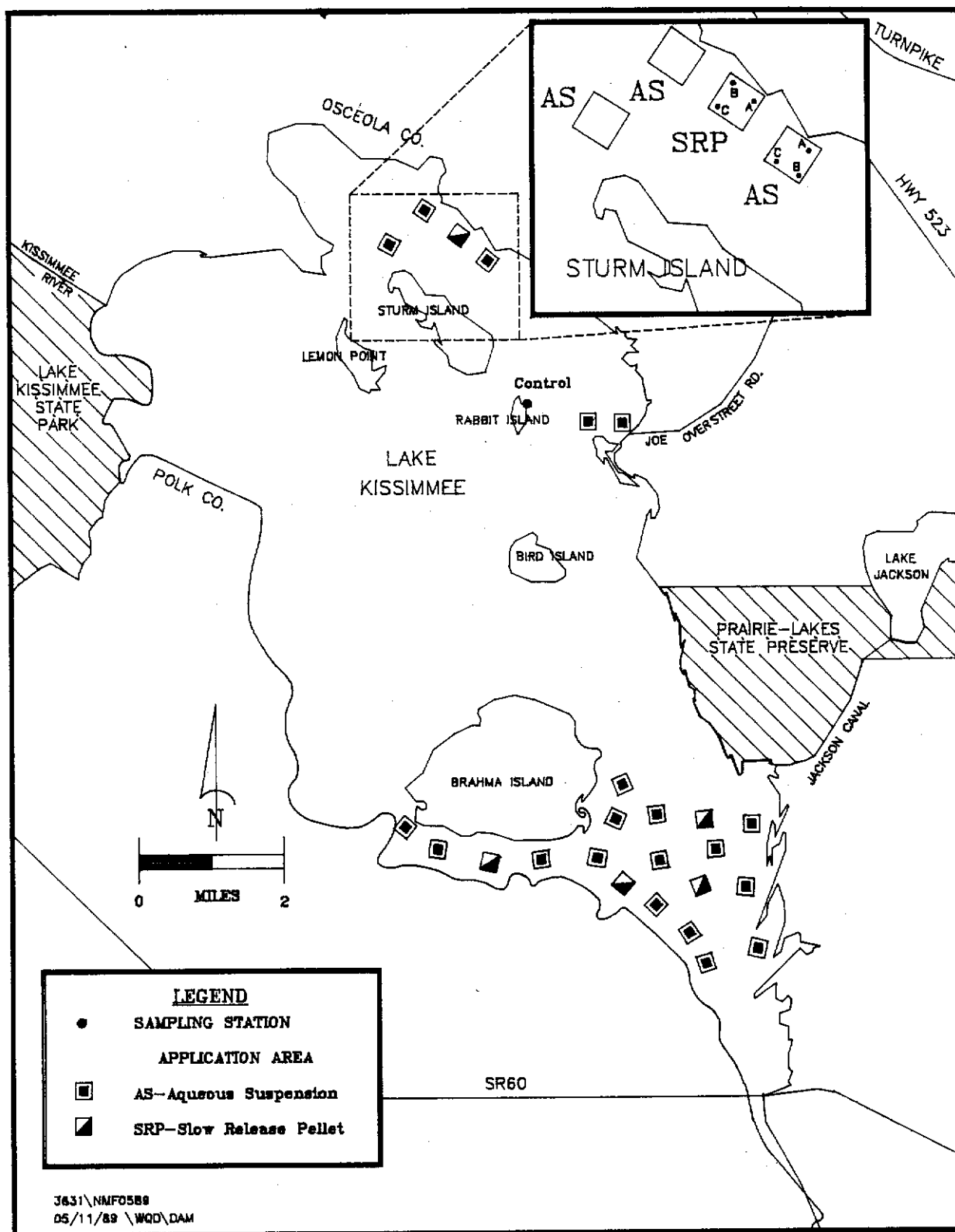
Figure 1. Fluridone and N-methylformamide Sampling Sites

TABLE 1. Sampling Frequencies at Fluridone Aqueous Suspension
Formulation Monitoring Site on Lake Kissimmee

Days Following Treatment	Water	Sediment
-1 (background-day before)	X	X
0 (day of treatment)	X	-
+ 1/16 (1.5 hours)	X	X
+ 1	X	X
+ 5	X	X
+ 8	X	X
+ 15	X	X
+ 22	X	X
+ 28	X	X
+ 35	X	X
+ 49	X	X
+ 119	-	X

TABLE 2. Sampling Frequencies at Fluridone Slow Release Pellet
Formulation Monitoring Site on Lake Kissimmee

Days Following Treatment	Water	Sediment
-1 (background-day before)	X	X
0 (day of treatment)	X	X
+ 3	X	X
+ 10	X	X
+ 17	X	X
+ 23	X	X
+ 30	X	X
+ 44	X	X
+ 114	-	X

was analyzed in the water samples up to 49 and 44 days after treatment at the aqueous suspension and pellet formulation sites, respectively. NMF analysis was restricted to the water samples since a sediment method has not been developed.

NMF and fluridone analysis was performed by the Environmental Laboratories Division (ELD) of Post, Buckley, Schuh and Jernigan, Inc. (PBS&J). This laboratory is certified by the Florida Department of Health and Rehabilitative Services for environmental water analysis. The ELD uses quality control/assurance protocols as outlined in a Florida Department of Environmental Regulation approved Generic Quality Assurance Plan (PBS&J, 1987). These protocols include performing duplicates and spikes at a frequency of one per batch or 10%, whichever is greater. Method blanks and internal standards are also carried through the entire preparation and analysis procedure. External and internal performance and system audits are also utilized.

A high performance liquid chromatography (HPLC) technique was used for the analysis of NMF and fluridone. The NMF procedure for the water samples consisted of filtering through a 0.45 micron filter and then directly being injected onto a C-18 HPLC column utilizing post column derivatization and fluorescence detection.

Conditions for the HPLC are as follows:

mobile phase: 95% sodium acetate 0.05 Normal/5% methanol
flow rate: 1.0 mL/min
injection volume: 500 uLs, for standards and samples
column: Sperisorb ODS-1, 4.6 mms by 25 cms 10 micron
detector: Milton Roy Fluoromonitor III, excitation-370 nanometers;
            emission-418 to 470 nanometers

Post column derivatization reagents are:
reagent A: 0.05 $\underline{N}$ sodium hydroxide
reagent B: 0.05 $\underline{N}$ sodium borate
            100 uL 2-mercaptoethanol in 1:1 acetonitrile
            100 mg o-phthaldehyde in 10 mL methanol

Post column derivatization heater was set at 95⁰C.

For the fluridone analysis, the water samples were analyzed by direct injection into the HPLC instrument after filtering through a 0.45 micron filter. The sediment extracts were cleaned by liquid-liquid partitioning and column chromatography for measurement by HPLC. Fifty grams of sediment were extracted with 2 $\underline{N}$ sodium hydroxide:methanol (1:1 v/v) by boiling for one hour. Upon cooling, methanol was added to bring the solution to the original volume and then the solution was vacuum-filtered through an 11-centimeter Buchner funnel fitted with a Whatman Number 42 filter paper. The extract was rotoevaporated to remove the excess methanol. This concentrated solution was transferred to a XAD-2 Column for cleaning. The column was washed with 40 mLs of 0.01 $\underline{N}$ sodium hydroxide:methanol (90:10 v/v) and the eluate discarded. The fluridone was eluted with 80 mLs of methanol. The methanol eluate was transferred to a 250 mL separatory funnel containing 100 mLs of 5% sodium chloride and 1 mL of 10% sodium hydroxide. The fluridone was extracted with three 40 mL aliquots of dichloromethane. The three dichloromethane extracts were combined by passing them through a Buchner funnel containing sodium sulfate (pre-washed with methanol) and collecting them in a 250 mL round bottom flask. The extract was rotoevaporated to dryness and redissolved with 5 mLs of hexane:dichloromethane (70:30 v/v). This extract was passed through an alumina column for cleaning. Three 5 mL portions of hexane:dichloromethane (70:30 v/v) were used to rinse the flask and then were added to the column. An additional 25 mL hexane:dichloromethane was used to rinse the column. A 20 mL and 50 mL column rinse with dichloromethane was performed. All combined extracts were rotoevaporated to dryness and redissolved with 5 mL of 65% methanol/35% water. This extract was filtered through a 0.45 micron filter and directly injected into the HPLC instrument.

7

Conditions for the HPLC are as follows:

mobile phase: 65% Methanol/35% water
flow rate: 1.0 mLs/min
sensitivity: 0.01 AUFS
injection volume: 500 uLs, for standards and samples
wavelength: 313 nanometers
chart speed: 0.5 cms/min
column: C8, Dupont Zorbax, 4.6 mm by 25 cm
column temperature: ambient

The calculations for fluridone are as follows:

$$fluridone\,(ppm) = \frac{PH1}{PH2}\,X\,\frac{V2}{V1}\,X\,\frac{Vf}{W}\,X\,\frac{Vt}{Va}\,X\,fluridone\,standard\,concentration$$

where:

PH1 is peak height of fluridone in sample in mm
PH2 is peak height of fluridone standard in mm
V1 is sample volume injected in uLs
V2 is standard volume injected in uLs
Vf is final volume of sample extract in mLs
Va is aliquot volume
Vt is total volume from which aliquot was taken
W is weight of sample analyzed
fluridone standard concentration is in nanograms/uL

8

RESULTS AND DISCUSSION

NMF was not detected in any of the water samples collected from either the treatment sites or the control site at a detection limit of 5 ppb. Theoretically, the maximum concentration of NMF which can be formed, based on molecular weight, is 18% of the fluridone present. Using the average value of 1,260 ppb of fluridone detected immediately after spraying at the aqueous suspension formulation site, it can be calculated that a 227 ppb level of NMF could potentially be present. This represents the worst case situation as the fluridone has not dispersed throughout the water column. Based on the application rate and a seven foot water depth, a calculated fluridone concentration of 133 ppb could be present, if upon application, the fluridone immediately dispersed throughout the water column. This would represent 24 ppb of NMF potentially being present. The 5 ppb detection limit would have been adequate to determine if NMF was being produced at the theoretical rate and persisting as indicated by the laboratory study of Saunders and Mosier (1983). In this field application study using the commercial formulations, NMF generation and persistence was non-detectable.

West, et al. (1988) evaluated NMF production in pond applications using both fluridone formulations applied at a rate similar to this study. The water concentrations of fluridone at the aqueous suspension treatment pond one day after treatment was only 77 ppb with the maximum observed level at 109 ppb, four days later. The highest fluridone concentrations in the water at the pellet formulation treatment pond was between 22 and 32 ppb, starting at 26 days after treatment. Both treatment sites continued to have detectable concentrations of fluridone 168 days after treatment. In both ponds, the initial fluridone levels were not as high as in this

study; however, fluridone residues persisted longer. Neither pond had a detectable NMF residue, at a detection limit of 2 ppb.

Although, in either situation (i.e., high initial levels, short duration versus low initial levels, long duration), photolysis is considered one of the major degradation pathways for fluridone (West, et al., 1979; Muir and Grift, 1982; Saunders and Mosier, 1983) and NMF one of the photodegradation products (Saunders and Mosier, 1983), NMF has not been found to be present in field applications. NMF does not appear to be a concern when fluridone is utilized in a lake application according to labeled rates.

The fluridone data obtained from the water and sediment sampling at the aqueous suspension formulation site are presented in Figures 2 and 3; the data from the pellet formulation site are presented in Figures 4 and 5. The control site monitoring results are presented in Figures 6 and 7. Data tables are presented in Appendix A.

The levels of fluridone detected in the water samples reflect what would be expected for this compound (Figures 2 and 4). Neither formulation site had detectable fluridone residues before treatment. The initial uneven dispersal of fluridone during the aqueous suspension formulation application is reflected in the varied results of the sampling done immediately after treatment. The aqueous suspension formulation site had the greatest quantities of fluridone detected during the day of application, with no detectable residues present after five days (Figure 2). At 22 days after spraying, a small peak in detectable quantities appeared. This peak has been attributed to a release of fluridone back into the water from stressed and
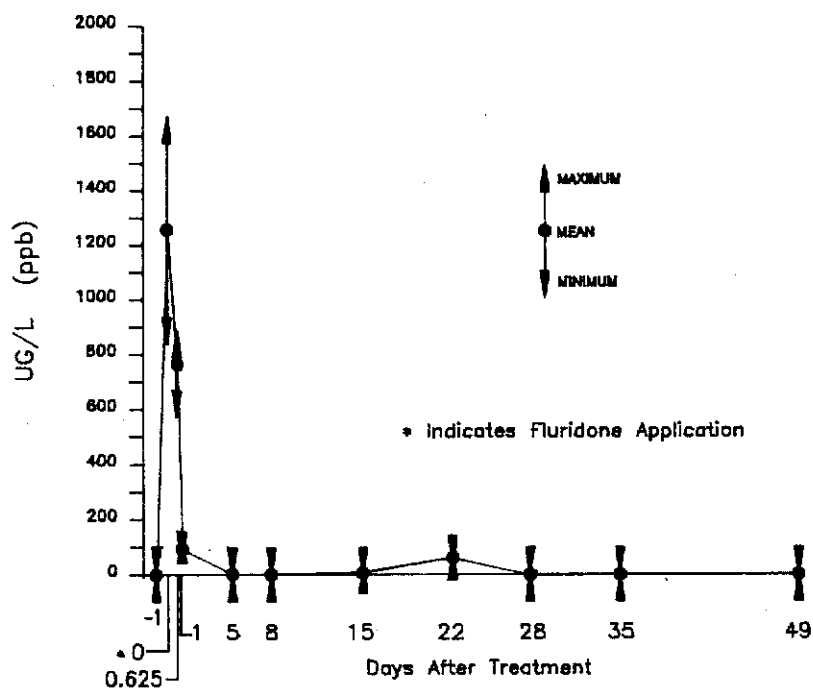
10

FIGURE 2. Fluridone Residues in Water Samples
from Aqueous Suspension Formulation Site.

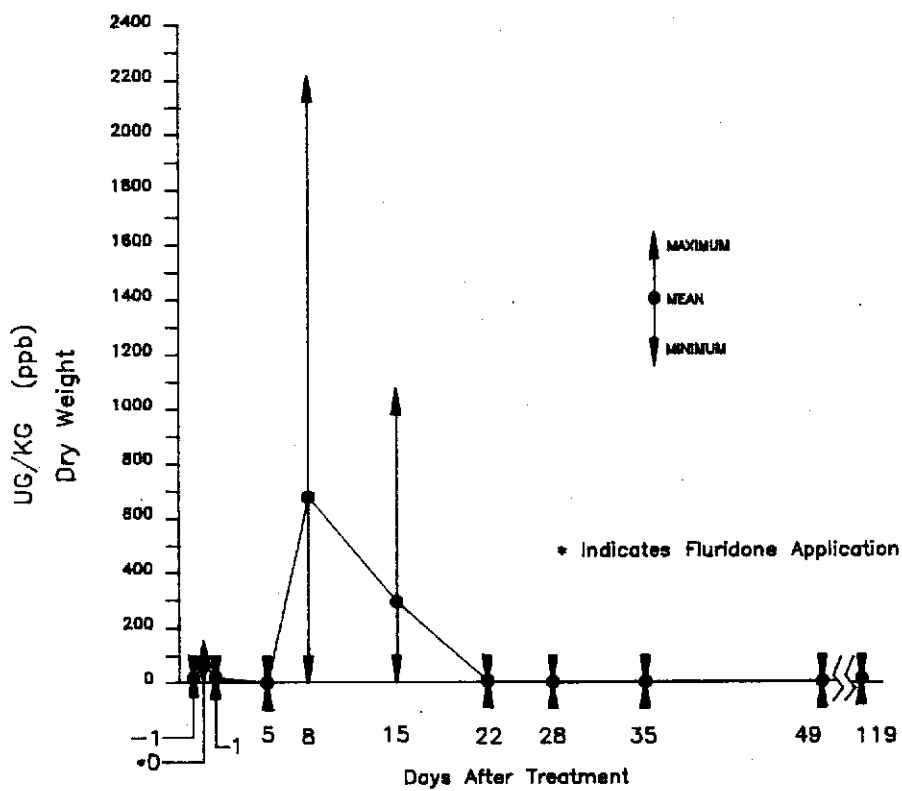FIGURE 3. Fluridone Residues in Sediment Samples
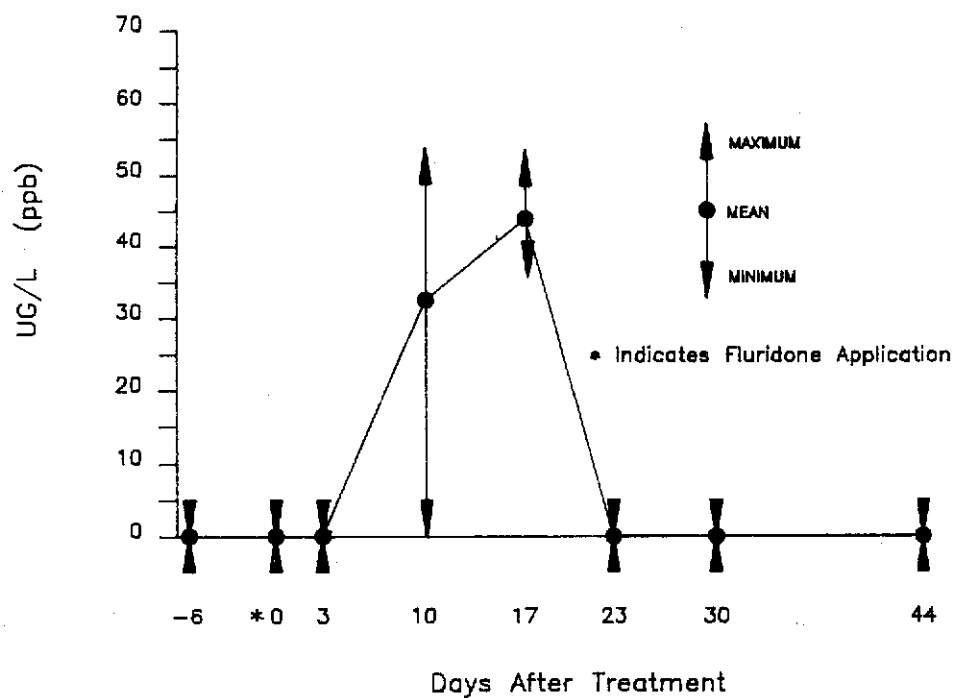from Aqueous Suspension Formulation Site.

11

FIGURE 4. Fluridone Residues in Water Samples
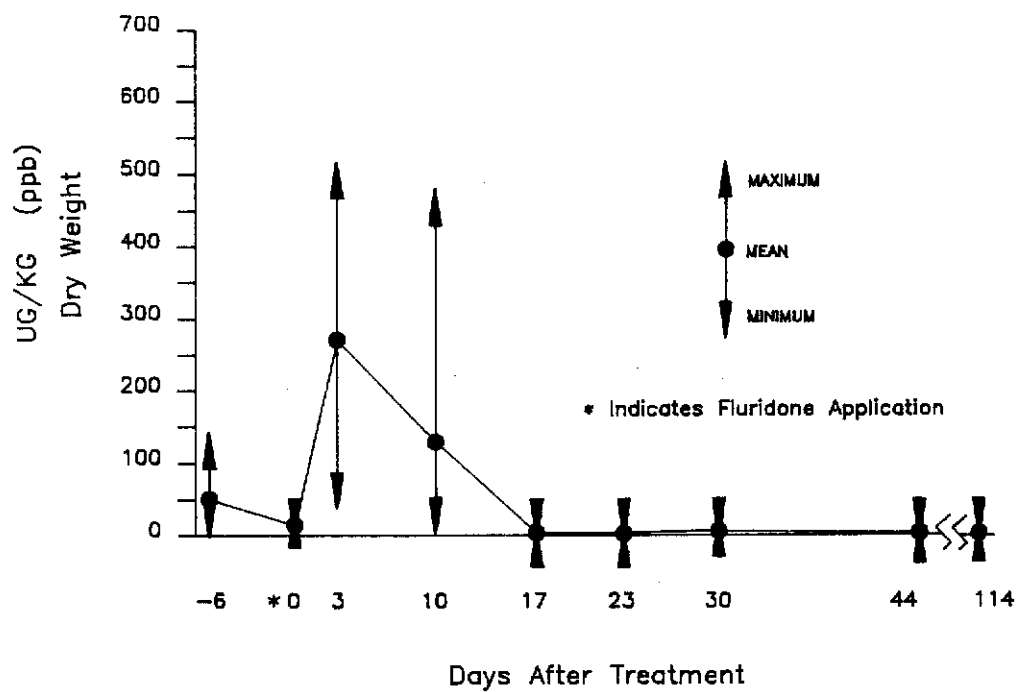from Pellet Formulation Site.

FIGURE 5. Fluridone Residue in Sediment Samples
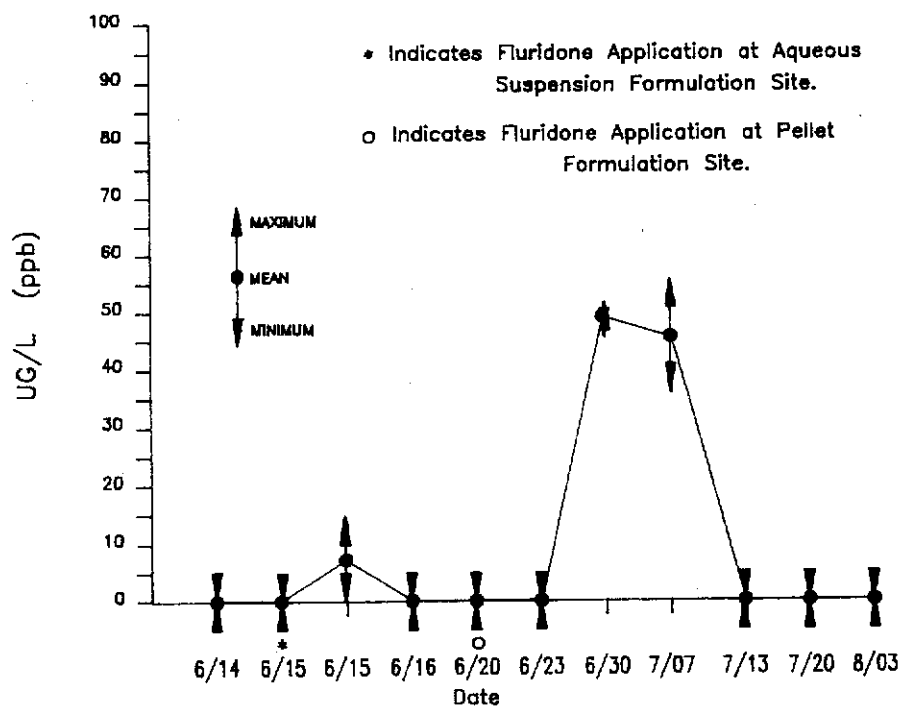from Pellet Formulation Site.

12

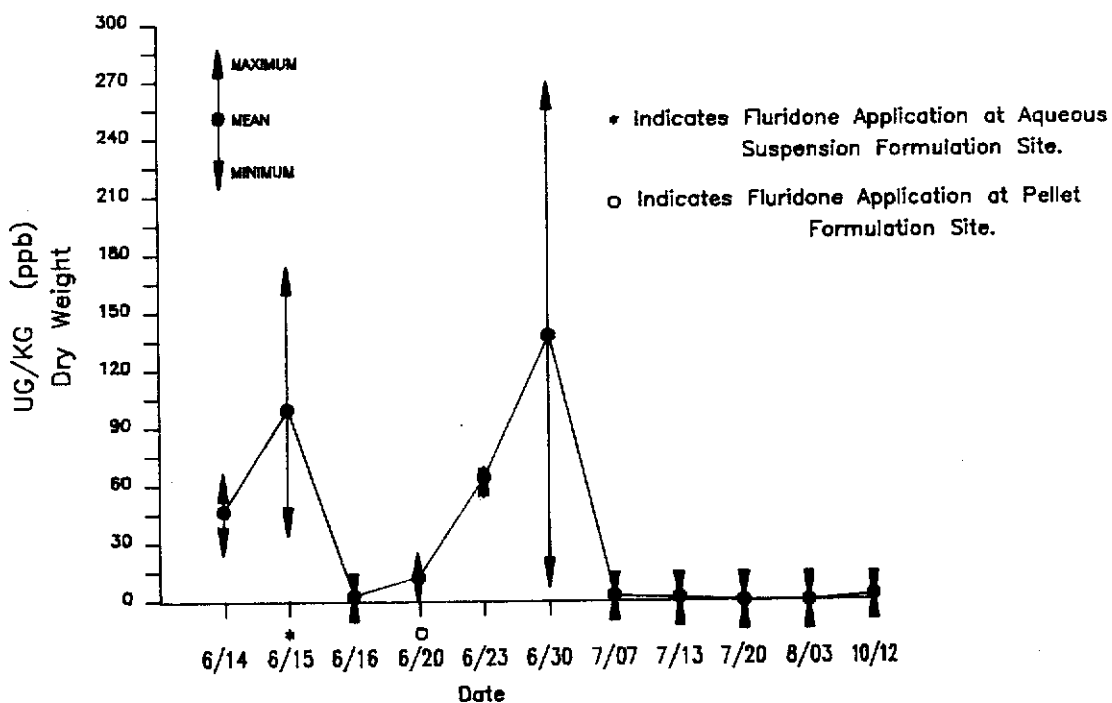FIGURE 6. Fluridone Residues in Water Samples from Control Site.

FIGURE 7. Fluridone Residues in Sediment Samples from Control Site.

13

decaying vegetation (Langeland and Warner, 1986; Pfeuffer, 1988). This peak was also detected in the water at the control site.

By plotting log percent of initial fluridone concentration remaining in the water versus time (in days), which follows pseudo-first order kinetics, the rate constant, k_1, can be determined by multiplying the slope of the line by -2.303. The units of k_1 are reciprocal time or day^{-1}. The half-life time was calculated according to the following equation: $t_{1/2} = 0.693/k_1$.

The half-life calculation is based upon percent of maximum concentration observed rather than percent of initial concentration due to uneven dispersal of the aqueous suspension formulation on the initial sampling date (West, et al., 1979). The field half-life of seven days was analogous to that reported in a similar monitoring program on Lake Okeechobee (Pfeuffer, 1988). True field half-life values cannot be estimated for lake trials because the dissipation is largely due to dispersal and dilution rather than degradation or sediment adsorption, especially when small areas are treated in large lakes. This is also supported by West, et al.(1983), who stated that applications of Sonar$^{(R)}$ to small plots (0.8 to 4.0 ha) in large lakes resulted in lower fluridone concentration and more rapid dissipation into the surrounding untreated water than when entire ponds were treated. Dispersal and dilution reduce the apparent half-life in lake water to less than one week (West, et al., 1983).

At the pellet formulation site, water column residues did not appear until 10 days after application (Figure 4). As expected, the fluridone took several days to be released from the clay pellets in levels sufficient for detection (West, et al., 1983; Langeland and Warner, 1986). The fluridone surface water residues were below detection limit 23 days after treatment. True half life values are difficult to

accurately estimate for lakes treated with the slow release pellet formulation because the fluridone concentration represents a net value reflecting both dissipation from the water, and the continued gradual release of more herbicide into the water as the clay pellets dissolved.

Detectable concentrations of fluridone were found in the sediment at the control, aqueous suspension, and pellet application sites before the spraying occurred on June 15 (Figures 3, 5, and 7). The average sediment residues peaked at 8 and 3 days after treatment at the aqueous suspension and pellet formulation sites, respectively. Both sites continued to have detectable residues at 119 and 114 days after treatment.

Fluridone has been found to persist in the sediment for long periods of time. Muir, et al. (1980) reported fluridone half-lives in the sediment to be greater than one year since relatively little change in herbicide concentration was seen after the maximum concentrations were reached. Similar persistence in sediment was noted by West, et al. (1979), who monitored fluridone residues up to 12 months after treatment at sites in Florida. Because fluridone is fairly persistent in sediment, the product label (i.e. Sonar(R)) permits the application of fluridone only once a year to a treatment site.

Previous fluridone applications occurred in Lake Kissimmee during June 1987, at seven 25-acre (10.1 hectare) sites. Six of the application areas were in the southern part of Lake Kissimmee, with the last area near the present study area. This application could be the source of the fluridone detected before the spraying occurred. However, since such a relatively small area of the lake was previously sprayed, the extent of the current background levels is hard to justify. The stability of fluridone in

15

the water and the release from decaying vegetation allows it to be transported outside the application area. The other potential source would be from the treatment plots in the southern part of Lake Kissimmee, sprayed the week before. In this case, fluridone would have had to rapidly migrate approximately 10 miles. Although fluridone does rapidly disperse throughout the water, movement over this distance is highly unlikely based on literature reports (West, et al., 1983; Pfeuffer, 1988).

CONCLUSION

NMF has not been found to be present in field applications of fluridone, although photolysis is considered one of the major degradation pathways for fluridone and NMF one of the photodegradation products. NMF does not appear to be a concern when fluridone is utilized in a lake application according to labeled rates.

The levels of fluridone detected in the water samples reflect what would be expected for this compound. The field half-life of seven days was analogous to that reported in a similar monitoring program on Lake Okeechobee.

REFERENCES

Baker, G. Operations and Maintenance Department, SFWMD, West Palm Beach,Florida Personal Communication, June 7, 1988

Barlow, S.M., and Sullivan, F.M. 1982. Reproductive Hazards of Industrial Chemicals:An Evaluation of Human and Animal Data, Academic Press, London England. pp. 346-359.

Kennedy, G.L. 1986. Biological Effects of Acetamide, Formamide, and Their Monomethyl and Dimethyl Derivatives. CRC Crit. Rev. Toxicol. 17:129-182.

Langeland, K.A. and Warner, J.P. 1986. Persistence of Diquat, Endothall, and Fluridone In Ponds. J. Aquat. Plant Manage. 24:43-46.

Muir, D.C.G., and Grift, N.P. 1982. Fate of Fluridone in Sediment and Water in Laboratory and Field Experiments. J. Agric. Food Chem. 30(2):238-244.

_____., Grift, N.P., Blouw, A.P. and Lockhart, W.L. 1980. Persistence of Fluridone in Small Ponds. J. Environ. Qual. 9(1):151-156.

Pfeuffer, R.J. 1988. Herbicide Monitoring Program for the Active Ingredient Fluridone [Sonar(R)]. South Florida Water Management District, West Palm Beach, Florida. Technical Publication 88-8.

Post, Buckley, Schuh and Jernigan, Inc. 1987. Generic Quality Assurance Project Plan. Orlando, Florida.

Saunders, D.G., and Mosier, J.W. 1983. Photolysis of the Aquatic Herbicide Fluridone in Aqueous Solution. J. Agric. Food Chem. 31(2):237-241.

West, S.D., Burger, R.O., Poole, G.M., and Mowrey, D.H. 1983. Bioconcentration and Field Dissipation of the Aquatic Herbicide Fluridone and Its Degradation Products in Aquatic Environments. J. Agric. Food Chem. 31(3):579-585.

_____., Day, E.W. Jr., and Burger, R.O. 1979. Dissipation of the Experimental Aquatic Herbicide Fluridone from Lakes and Ponds. J. Agric. Food Chem. 27(5):1067-1072.

_____., Langeland, K.A., and Laroche, F.B. 1988. Analytical Results from the Determination of Fluridone and N-Methylformamide in Pond Water Treated with the Aquatic Herbicide Sonar(R), Initial Report. Lilly Research Laboratories, Greenfield In.

APPENDIX A

Fluridone Water and Sediment Residues

TABLE A-1. Concentration of Fluridone Residues at Aqueous Suspension Formulation Site.

sampling date	days after treatment	water μg/L station				sediment μg/Kg dry weight station			
		A	B1	B2	C	A	B1	B2	C
6/14	pretreatment	BDL	BDL	BDL	BDL	27.9	49.9	BDL	BDL
6/15	0	840	1350	1170	1680	NS	NS	NS	NS
6/15	1/16	570	730	880	890	101.0	9.4	158.0	BDL
6/16	1	140	59	90	62	29.9	BDL	42.0	BDL
		150[a]			64[a]	7.8[a]			41.7[a]
6/20	5	BDL	BDL	BDL	BDL	BDL	BDL	3.8	BDL
6/23	8	BDL	BDL	BDL	BDL	BDL	2220.0	480.0	10.8
6/30	15	BDL	BDL	BDL	31	100.0	2.2	3.1	1080.0
7/7	22	80	70	59	44	10.6	5.6	BDL	6.2
7/13	28	BDL	BDL	BDL	BDL	BDL	3.7	BDL	BDL
7/20	35	BDL	BDL	BDL	BDL	BDL	BDL	2.7	3.3
8/3	49	BDL	BDL	BDL	BDL	3.6	BDL	4.3	BDL
10/12	119	NS	NS	NS	NS	15.3	BDL	12.5	13.9

Key: "BDL" Residue below detection limit of 5 μg/L for water samples and 2.0 μg/Kg for sediment samples.

"NS" Station not sampled.

[a] Station duplicate

TABLE A-2. Concentration of Fluridone Residues at Pellet Formulation Site.

sampling date	days after treatment	water µg/L station				sediment µg/Kg dry weight station			
		A	B1	B2	C	A	B1	B2	C
6/14	pretreatment	BDL	BDL	BDL	BDL	BDL	144.0	8.7	49.9
6/20	0	BDL	BDL	BDL	BDL	BDL	BDL	26.0	34.0
6/23	3	BDL	BDL	BDL	BDL	420.0	108.0	36.9	518.0
6/30	10	28	BDL	54	49	11.1	2.7	26.5	480.0
7/7	17	46	41	36	54	BDL	4.5	6.7	4.6
7/13	23	BDL	BDL	BDL	BDL	4.2	BDL	2.6	5.7
7/20	30	BDL	BDL	BDL	BDL	BDL	BDL	20.8	6.1
8/3	44	BDL	BDL	BDL	BDL	BDL	4.6	BDL	11.1
10/12	114	NS	NS	NS	NS	12.7	BDL	BDL	BDL

Key: "BDL" Residue below detection limit of 5 µg/L for water samples and 2.0 µg/Kg for sediment samples.

"NS" Station not sampled.

20

TABLE A-3. Concentration of Fluridone Residues at Control Site.

sampling date	days after treatment	water µg/L Site 1	Site 2	sediment µg/Kg dry weight Site 1	Site 2
6/14	pretreatment	BDL	BDL	66.0	27.9
6/15	0	BDL	BDL	NS	NS
6/15	1/16	15	BDL	35.9	176.0
6/16	1	BDL	BDL	BDL	3.6
6/20	5	BDL	BDL	BDL	28.0
6/23	8	BDL	BDL	72.0	54.0
6/30	15	52	46	6.7	270.0
7/7	22	56	36	BDL	4.6
7/13	28	BDL	BDL	BDL	3.3
7/20	35	BDL	BDL	BDL	BDL
8/3	49	BDL	BDL	BDL	BDL
10/12	119	NS	NS	5.8	BDL

Key: "BDL" Residue below detection limit of 5 µg/L for water samples and 2.0 µg/Kg for sediment samples.

"NS" Station not sampled.

21